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FASIL INTEGRAL FUEL TANK SEALANTS. PART I.(U)
JAN 79 O R PIERCE, K M LEE, K ROSSKNECHT

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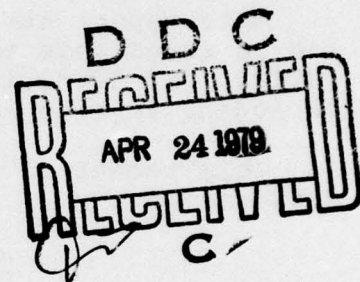
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FASIL INTEGRAL FUEL TANK SEALANTS

Dow Corning Corporation
Midland, Michigan 48640



January 1979
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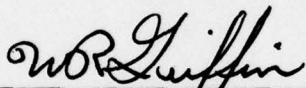
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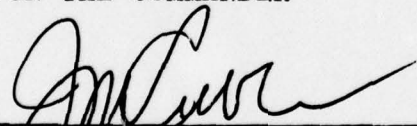
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W. R. GRIFFIN
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FOR THE COMMANDER



J. M. KELBLE, Chief
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Channel sealant	Silanes	
Sealant	Silphenylenes	
Polymer	Metadibromobenzenes	
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<p>1. Several reactive silphenylene intermediates, i.e. m-[XSiMe(CH₂CH₂CF₃)]₂C₆H₄, where X=Cl, H, OMe and OC₂H₅, were prepared via Grignard reactions of metadibromobenzene and various fluoroalkylsilanes. Optimization of yield was accomplished by studying the effects of stoichiometry, mode of addition, solvent, magnesium conditioning, and work up procedures. Several of the by-products occurring in these systems were isolated and characterized. More than 4500 g. of m-silphenylenes were prepared.</p>		

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2. Two attempts were made to prepare m-silphenylenes via organolithium reactions.

3. The conversion of these silphenylenes to silanols was studied by hydrolysis of SiOR, and by hydrolysis of SiH via active metal catalysts. The latter gave the best purity, reproducibility and volume efficiency.

4. Reactive fluoroalkyldisiloxanes, i.e. $[\text{XSiMe}(\text{CH}_2\text{CH}_2\text{CF}_3)]_2\text{O}$,

were prepared where X=Cl, OH, $\text{N}-\overset{\text{Me}}{\underset{|}{\text{C}}}-\overset{\text{O}}{\parallel}-\text{Me}$, NMe_2 , and $\text{N}(\text{C}_6\text{H}_5)\overset{\text{O}}{\parallel}-\text{NMe}_2$.

5. Metasilphenylene disilanol was combined with reactive disiloxanes to produce FASIL copolymers of low molecular weight. Three samples were submitted to AFML for evaluation.

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PREFACE

This report was prepared by the Contract Research Laboratory, Dow Corning Corporation, Midland, Michigan under Contract No. F33615-77-C-5139 and covers the period 1 September, 1977 to 31 August, 1978. The sponsoring agency is the Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio. The Project Engineer is Mr. W. R. Griffin (MBT).

The personnel of Dow Corning Corporation assigned to this project are the following: Dr. O. R. Pierce (Principal Investigator), Mr. K. M. Lee (Project Specialist), Miss K. Rossknecht (Assoc. Chemist) and Dr. A. H. McHale (Project Chemist).

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SUMMARY

1. Several reactive silphenylene intermediates, i.e. m-
 $[\text{XSiMe}(\text{CH}_2\text{CH}_2\text{CF}_3)]_2\text{C}_6\text{H}_4$ where X=Cl, H, OMe and OC_2H_5 , were prepared via Grignard reactions of metadibromobenzene and various fluoroalkylsilanes. Optimization of yield was accomplished by studying the effects of stoichiometry, mode of addition, solvent, magnesium conditioning, and work up procedures. Several of the by-products occurring in these systems were isolated and characterized. More than 4500 g. of m-silphenylenes were prepared.
2. Two attempts were made to prepare m-silphenylenes via organolithium reactions.
3. The conversion of these silphenylenes to silanols was studied by hydrolysis of SiOR, and by hydrolysis of SiH via active metal catalysts. The latter gave the best purity, reproducibility and volume efficiency.
4. Reactive fluoroalkyldisiloxanes, i.e. $[\text{XSiMe}(\text{CH}_2\text{CH}_2\text{CF}_3)]_2\text{O}$,

$\begin{array}{c} \text{Me} \quad \text{O} \\ | \quad || \\ \text{N}-\text{C}-\text{Me} \end{array}$

 were prepared where X= Cl, OH, $\begin{array}{c} \text{O} \\ || \\ \text{N}(\text{C}_6\text{H}_5)\text{C}-\text{NMe}_2 \end{array}$, and $\text{N}(\text{C}_6\text{H}_5)\text{C}-\text{NMe}_2$.
5. Metasilphenylene disilanol was combined with reactive disiloxanes to produce FASIL copolymers of low molecular weight. Three samples were submitted to AFML for evaluation.

INTRODUCTION

The objective of this three year program is the synthesis, formulation, and evaluation of FASIL (fluoroalkylarylene-siloxanylene) copolymers as curing and non-curing seals for fuel containment in high performance aircraft.

This portion of the program was concerned primarily with the synthesis of monomers but a brief examination of selected polymerization systems was also conducted.

Polymers containing the silphenylene structure have attracted the attention of a number of workers over the past twenty years because their thermooxidative stability¹ is superior to that of $(\text{Me}_2\text{SiO})_x$. Copolymers of silphenylenes and dimethylpolysiloxanes were envisioned as materials possibly possessing the desirable properties of both parent systems and this was realized to a certain extent. Thus incorporating silphenylene units into polydimethylsiloxane decreases the tendency to split out cyclic oligomers in a hot environment but raises the T_g because silphenylene tends to be crystalline. Most of the early examples contained the structure $-(\text{OMe}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiMe}_2)_n-$, i.e. only methyl groups on silicon and only para substitution. Key publications which reference most of the important early synthetic and polymer characterization work in this area and have the greatest impact on the present study are those of Merker and Scott¹, and Patterson, McManus, and Pittman². The latter study is especially instructive because it deals with optimum conditions for polymerization via aminosilane and silanol reactions — the method adopted and recommended by AFML personnel — and importantly, T_g effects as a function of composition.

Examples of silphenylene monomers, polymers and copolymers which contain fluorine are few and those with metasilphenylene structure are fewer still, however, some related background does exist.

Borisov³, prepared $-\text{[SiMe(CH}_2\text{CH}_2\text{CF}_3\text{)OSiMe(CH}_2\text{CH}_2\text{CF}_3\text{)-}\langle\bigcirc\rangle\text{-SiMe-CH}_2\text{CH}_2\text{CF}_3\text{)]}_n\text{-}$ and reported that substitution of polar groups such as $\text{CH}_2\text{CH}_2\text{CF}_3$ for CH_3 raises the T_g . He also determined that para-silphenylenes increase T_g values much more than meta silphenylenes.

Odabashyan⁴ and Coworkers prepared a series of p-silphenylenes, $(\text{CF}_3\text{CH}_2\text{CH}_2)\text{RHSi}-\langle\bigcirc\rangle\text{-SiHR(CH}_2\text{CH}_2\text{CF}_3\text{)}$, where $\text{R} = \text{Me, Et, nPr, CH}_2\text{CH}_2\text{CF}_3$, and \emptyset . No polymers were reported.

Loree⁵ reported polymers and copolymers containing

$\text{[(CF}_3\text{CH}_2\text{CH}_2\text{)MeSi}-\langle\bigcirc\rangle\text{-SiMe(CH}_2\text{CH}_2\text{CF}_3\text{)O}]_n\text{-}$, and concurrently

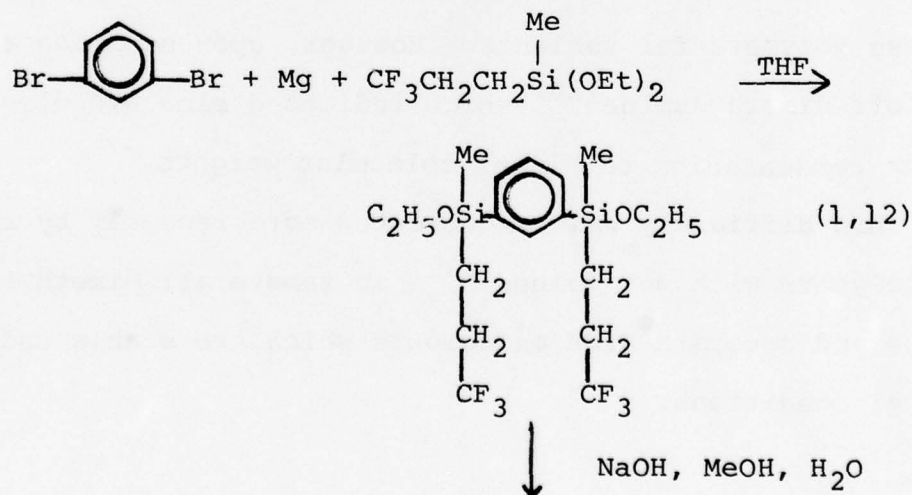
Grindahl⁶ patented compositions containing $\text{[Me(CF}_3\text{CH}_2\text{CH}_2\text{)Si}-\langle\bigcirc\rangle\text{-Si(CH}_2\text{CH}_2\text{CF}_3\text{)MeO}]_n\text{-}$.

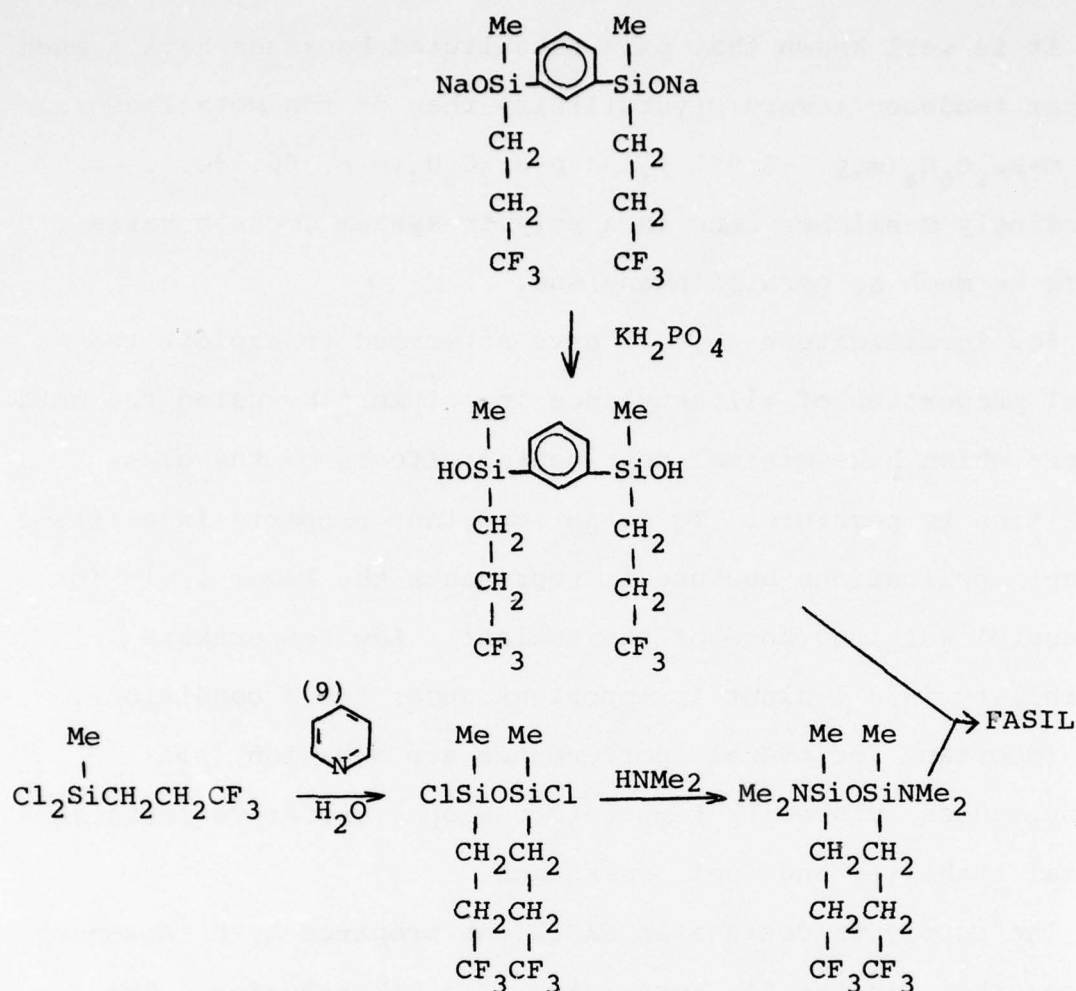
Patterson and Morris⁷ prepared polymers containing perfluoroalkylene units in the backbone, $\text{[Me}_2\text{Si}-\langle\bigcirc\rangle\text{-(CF}_2\text{)}_n\text{-}\langle\bigcirc\rangle\text{-SiMe}_2\text{O}]_x\text{-}$, where $n = 3$ and 6 .

It is well known that para substituted benzenes have a much greater tendency toward crystallinity than do the meta isomers, e.g. m-Br₂C₆H₄ (m.p. -6.9°C.) and p-Br₂C₆H₄ (m.p. 86.9°C.). Accordingly m-silphenylene in a polymer system doesn't raise the T_g as much as para silphenylene.

Very few investigators (5,6,8) have attempted to exploit the useful properties of silphenylenes in polymers by using the meta isomers which have minimal detrimental effects on the glass transition temperature. T_g is an important property in airframe sealant applications because it represents the lower limit for the useful working range of the sealant. Low temperature flexibility in a sealant is important under Arctic conditions. Also important for overall performance are adhesion, non-corrosiveness, viscosity-temperature slope, oxidative resistance, thermal stability and fuel resistance.

The copolymer designated FASIL was prepared by H. Rosenberg and coworkers in the Air Force Materials Laboratories. The preparative chemistry involved the following scheme⁸.





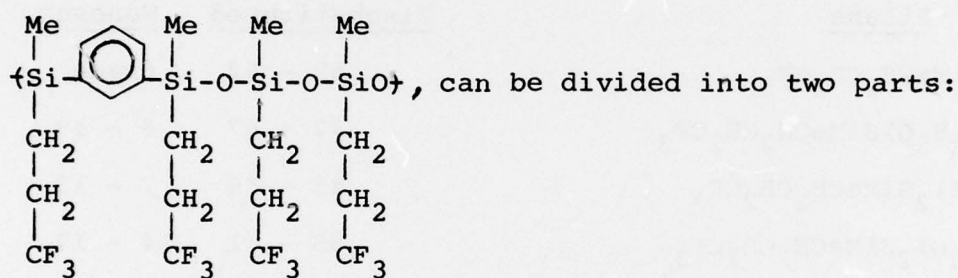
The early samples prepared by this method showed promise as base polymers for sealants. However, upon standing the polymers gave off dimethylamine⁽¹⁰⁾ which indicated slow hydrolysis and/or condensation to higher molecular weights.

This difficulty was circumvented more recently by refluxing the polymers with wet toluene⁽¹¹⁾ to remove all dimethylamino groups and generate SiOH end groups which are stable under neutral conditions.

II. DISCUSSION

The early part of this program was concerned with preparing and stockpiling intermediates which react to give polymers. Although procurement of significant quantities of the reactive intermediates was a primary objective, optimization of the preparative methods was deemed important since the later stages of this program would involve preparing much larger quantities of the finalized formulations.

The synthesis of the monomers which react to produce FASIL,

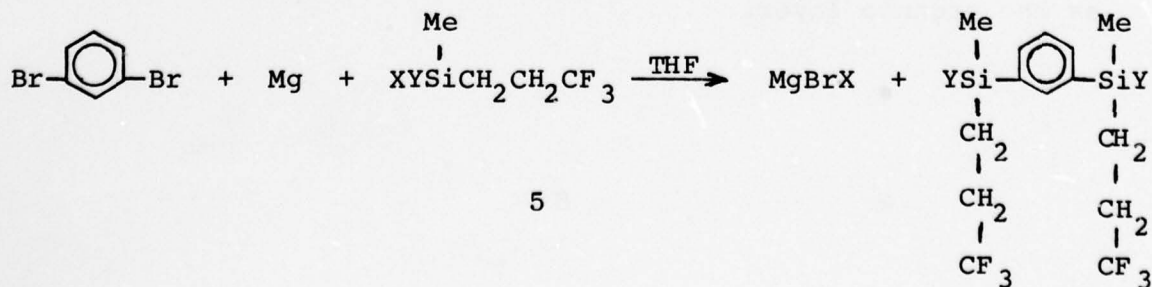


(A) synthesis of reactive metasilphenylenes and (B), synthesis of reactive fluoroalkyldisiloxanes. Part C is concerned with exploratory polymerizations.

A. Synthesis of Reactive Metasilphenylenes

In this program the Grignard reaction is the only method used extensively to prepare m-silphenylene. Organolithium systems were investigated briefly but exploratory departures from the Grignard methods recommended by AFML personnel⁸ were deferred until later in the program - time and other factors permitting.

The basic system is shown below:



X and Y may be the same or different. The silanes employed in this scheme were $X = Y = \text{Cl}$, $X = Y = \text{OC}_2\text{H}_5$, $X = Y = \text{OCH}_3$, $X = \text{Cl}$ and $Y = \text{H}$, and $X = \text{OC}_2\text{H}_5$ and $Y = \text{Cl}$. Results of the Grignard reactions appear in Table 1. The "in situ" technique is a necessity in these systems to minimize side reactions. It consists of adding m-dibromobenzene in tetrahydrofuran to a pot containing tetrahydrofuran, silane in excess of the halide, and magnesium. The yields of m-silphenylene obtained from the various silanes are as follows:

<u>Silane</u>	Yield - Mole %	
	<u>Disubstituted</u>	<u>Monosub.</u>
$\text{Cl}_2\text{SiMeCH}_2\text{CH}_2\text{CF}_3$	59 - 62	trace
$\text{Cl}(\text{C}_2\text{H}_5\text{O})\text{SiMeCH}_2\text{CH}_2\text{CF}_3$	42 - 67	6 - 19
$(\text{CH}_3\text{O})_2\text{SiMeCH}_2\text{CH}_2\text{CF}_3$	45 - 59	7 - 13
$(\text{C}_2\text{H}_5\text{O})_2\text{SiMeCH}_2\text{CH}_2\text{CF}_3$	55 - 71	14 - 17
$\text{HClSiMeCH}_2\text{CH}_2\text{CF}_3$	62 - 80	trace

Dialkoxysilanes require temperatures of at least 55°C for coupling to occur and $60 - 65^\circ\text{C}$ seems optimum. The halosilanes can be run at room temperature or lower, $15 - 20^\circ\text{C}$.

The salts obtained as by-products are easiest to handle in the systems containing chlorosilanes. With alkoxysilanes the salts have some organic character, less crystallinity and are more difficult to remove by filtration. The system based on 3,3,3-trifluoropropylmethylchlorosilane has an advantage in that the salts can be dissolved in water and the products removed as the organic layer.

The excess of silane was varied over a range of 50 mole percent to 500 mole percent, but definite trends are difficult to discern without several runs at each level.

MOLE % EXCESS SILANE (HClMeSiCH ₂ CH ₂ CF ₃)	% YIELD	# OF RUNS
100	70-75	2
200	62-76	6
300	78	1
500	80	1

It appears that there is no advantage to the use of more than 100% excess silane. Also, large excesses of silane undoubtedly lessen the ability of tetrahydrofuran to dissolve salts.

The molar ratio of RMgX to THF was varied from 7.2 to 16.6. Kharasch and Reinmuth¹³ recommended at least 6 THF to 1 ϕ Br for optimum yield and this was considered the minimum level since silane decreases the solvent power. Most of the Grignard work reported here was done with 8.0 to 8.4 moles of tetrahydrofuran to 1 RMg- and the few runs made with higher levels of solvent seemed to offer no distinct advantage.

Diethylether and triethylamine were both tried as solvents for the Grignard reaction, but neither one would promote reaction at room temperature or up to 60°C.

It was discovered that freshly pulverized (Waring blender) magnesium greatly facilitated reaction and allowed better control of temperature in the reaction of dialkoxysilane and metadi-bromobenzene, where exotherms were occasionally experienced. No such problems were encountered with the chlorosilane.

Exchange of negative groups on silicon was observed in the reaction of $\text{CF}_3\text{CH}_2\text{CH}_2\text{MeSiHCl}$ with metadibromobenzene. This was evidenced by the isolation of 3,3,3-trifluoropropylmethylsilane ($\text{CF}_3\text{CH}_2\text{CH}_2\text{MeSiH}_2$) during solvent recovery and by the acidity of the product, i.e. the m-bis(3,3,3-trifluoropropylmethylhydrido-silyl)benzene was contaminated with Si-Cl. When some of sample 3,3,3-trifluoropropylmethylchlorosilane was heated with salts obtained from a Grignard reaction no 3,3,3-trifluoropropylmethylsilane formed. Apparently the exchange takes place during the actual coupling reaction.

Organometallic syntheses in general are characterized by poor volume efficiency, troublesome salt formation and tedious manipulations. Significant amounts of product are usually occluded in the salts and the recovery of this is worthwhile.

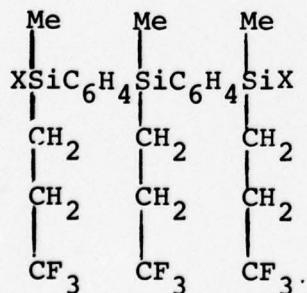
Filtration and washing with solvent does a fair job of removing product from magnesium halides but is difficult to manage with magnesium alkoxides. A extraction apparatus was set up (See Figure 2) which minimized the handling involved in recovering product from the salts. Solvent and excess silane were flash-distilled from the salts which were dumped into the extractor with fresh diethylether. The extractor was typically run overnight with the products accumulating in the overflow pot.

Salts from Grignard reactions of silanes such as R_2SiHCl can be worked up with water since the product isn't easily hydrolyzable.

The hydride system was the only one which gave no mono-substituted materials in the product mix. With the other silanes it appears that every possible product occurs. Thus during a Grignard run a sample was withdrawn and treated with excess dimethylchlorosilane. The resulting products were examined by GLC - Mass Spectral Analysis. The following is a partial list of the compounds present with an indication of how the product arose:

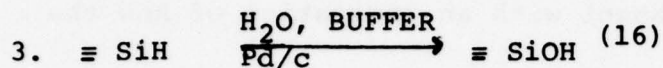
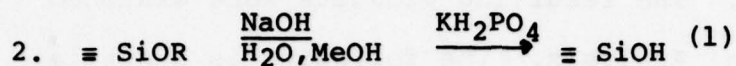
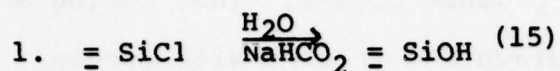
$(\text{Me}_2\text{HSi})_2\text{O}$	(chlorosilane & moisture)
BrC_6H_5	(reduction product)
$\text{Me}_2\text{HSiC}_6\text{H}_5$	(reduction product)
$m\text{-Br}_2\text{C}_6\text{H}_4$	(starting material)
$\text{HMe}_2\text{SiC}_6\text{H}_4\text{Br}$	(monsubstitution)
$\text{BrC}_6\text{H}_4\text{OH}$	($\text{RMgBr} + \text{O}_2$)
$\text{HMe}_2\text{SiOC}_6\text{H}_4\text{SiMe}_2\text{H}$	(monsubstituted phenol + chlorosilane)
$\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$	($\text{RMgBr} + \text{BrC}_6\text{H}_4\text{Br}$, reduction)
$\text{HMe}_2\text{SiC}_6\text{H}_4\text{SiMe}_2\text{H}$	(disubstitution - major product)

In all the systems the most prevalent by-product was



where X varies with the starting silane.

Three methods were available for converting reactive silphenylenes to silanols:



The first method was not employed in this study because the Grignard route to the silphenylene chloride gave relatively low yields and was not used. Also, contamination by chloride ion is very undesirable in applications involving titanium surfaces.

Method 2 was examined and it does give the desired silanols but frequently the product is contaminated with alkoxy groups which act as end blocking group during polymerization.

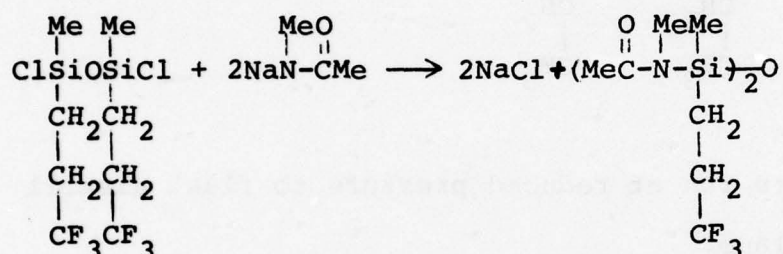
The third method is clearly the one of choice in terms of reproducibility, volume efficiency and quality of product. Neutral conditions are maintained throughout the preparation.

B. Synthesis of Reactive Fluoroalkyldisiloxanes

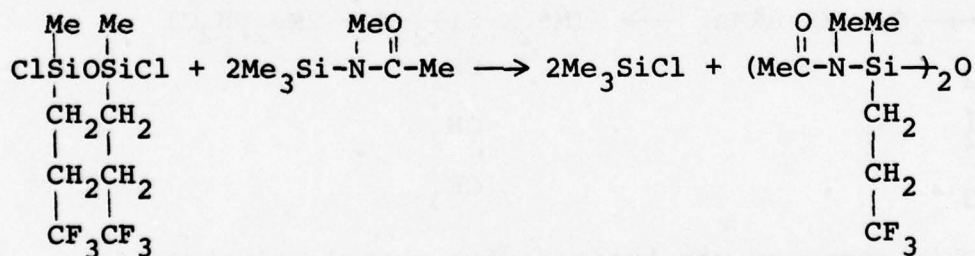
The reactive disiloxanes employed in this study were prepared by relatively straightforward reactions which appear in the experimental. No studies were conducted to optimize yields.

Symmetrical bis(3,3,3 trifluoropropyl)dimethyldichlorodisiloxane was available from an earlier study¹⁴.

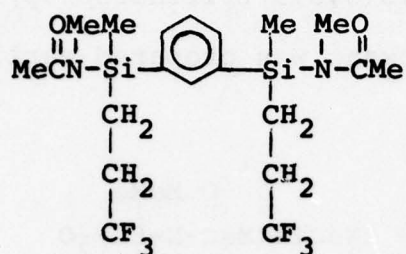
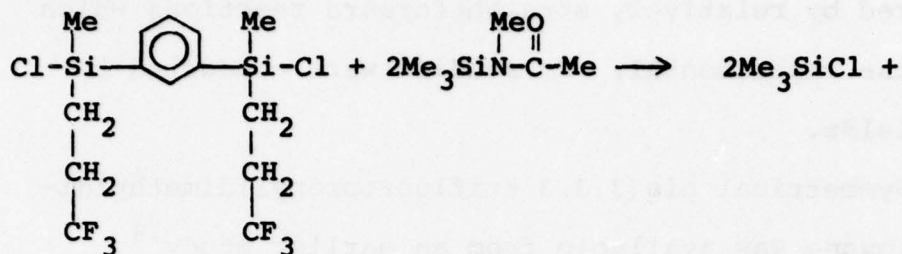
Symmetrical bis(3,3,3 trifluoropropyl)bis(N-methylacetamido)dimethyldisiloxane was prepared earlier¹⁴ by the following reaction:



Due to the unavailability of the sodium salt, for the present study this compound was prepared by the following exchange reaction which worked well.

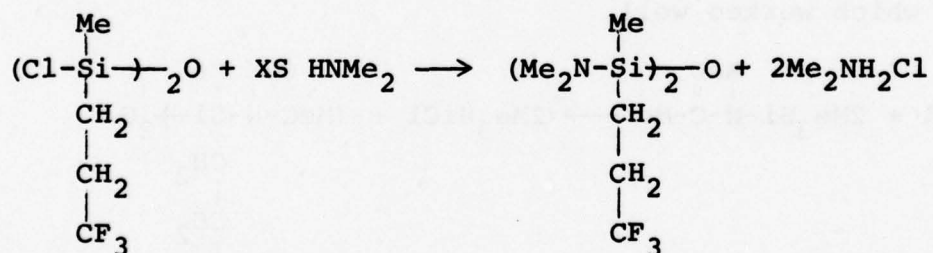


The same exchange system was applied as follows:

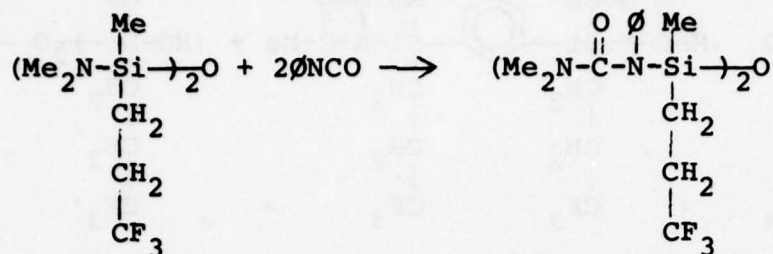


These exchanges are run at reduced pressure to flash distill trimethylchlorosilane.

Symmetrical bis(dimethylamino)dimethyl-bis(3,3,3 trifluoropropyl)disiloxane was prepared by the following straightforward reaction:



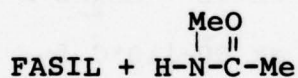
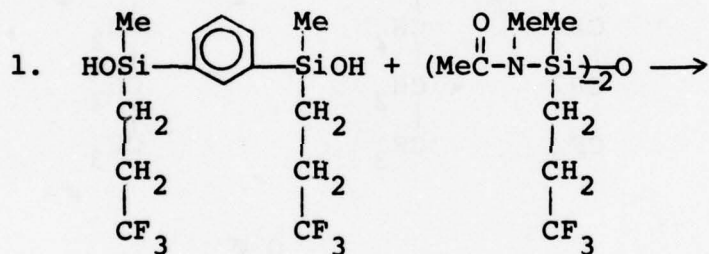
This compound was treated with phenylisocyanate to produce the ureido derivative.



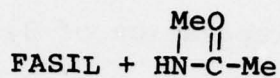
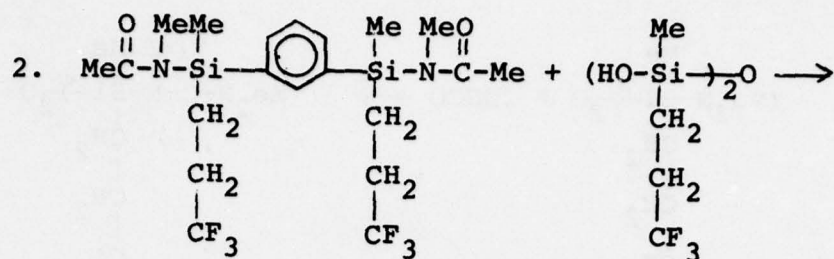
During the preparation of 3,3,3 trifluoropropylmethyl-diethoxysilane some disiloxane and trisiloxane were produced and these were isolated and characterized.

C. Polymerizations

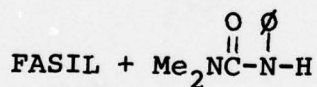
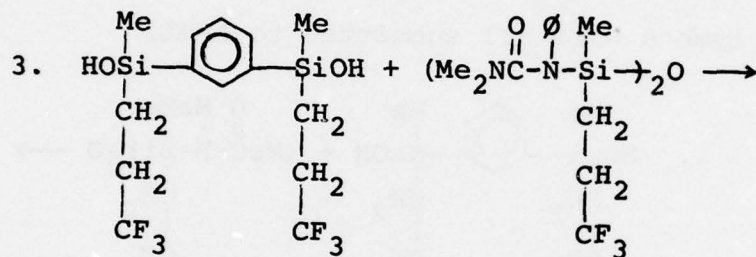
Polymerizations were carried out with the following systems to establish feasibility - no optimization was done. These polymers were all submitted to AFML.



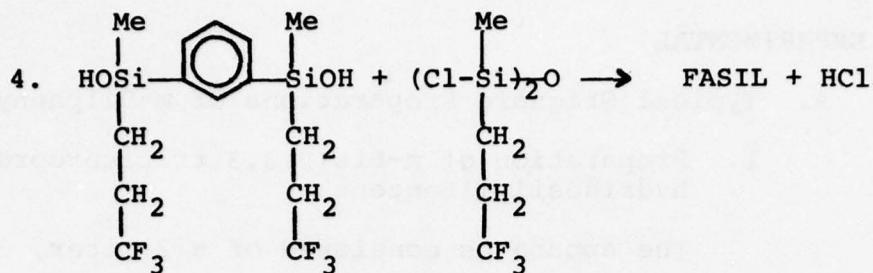
This system exhibited a mild exotherm when first mixed but the reaction quickly slowed. Repeated heat treatments at 100° followed by devolatilization produced increases in viscosity but the system seemed rather unreactive. A polymer of ~2900 cs was produced.



An exotherm was also noted in this reaction but again extended heating under vacuum was required to keep the reaction going and only low molecular weight was achieved.



Heating at 80-110°C for 8 hours gave a polymer which was almost non-flowing but cloudy.



This reaction produced a low viscosity fluid after 24 hours at 90-135°C. The fluid was treated with water followed by heating with a condensation catalyst which greatly increased the viscosity.

These reactions demonstrated the feasibility of making polymer by these methods. Further work will be done to select the best overall method for making FASIL.

III. EXPERIMENTAL

A. Typical Grignard Preparations of m-Silphenylenes

1. Preparation of m-Bis(3,3,3 trifluoropropylmethylhydridosilyl)benzene

The apparatus consisted of a 2 liter, 3 necked flask equipped with a water cooled condenser, pressure-equalized addition funnel, thermometer, and an air driven Hershberg stirrer. The components were oven dried at 150°C for a minimum of 2 hours, assembled hot and allowed to cool with dry nitrogen flowing through a T-tube vent atop the condenser.

The pot was charged with 36.5 g (1.5 moles) of freshly pulverized magnesium turnings*, 531.0 g (3.0 moles) of 3,3,3 trifluoropropylmethylchlorosilane and 451 ml of tetrahydrofuran. This mixture was stirred vigorously while a solution of 118.0 g (0.5 moles) of m-dibromobenzene and 226 ml of tetrahydrofuran was added dropwise over a period of 2 hours. The temperature was maintained between 15 and 20°C. After the addition was completed the system was stirred for one hour.

Tetrahydrofuran and excess silane were removed with a rotary evaporator to a final condition of 45°C at 1 mm of Hg. The products were diluted with 500 ml dry diethylether and transferred to pot "A" of an extraction apparatus. See Figure 1. The receiver F of the extraction apparatus was charged with 300 ml of dry diethylether and warmed to boiling.

* Magnesium turnings were dried at 150°C for 30 minutes and then pulverized in a Waring Blender at "whip" speed for 3 minutes.

The extraction was run for 24 hrs. The ethereal solution of products from F was filtered and distilled to give 126.5 g (0.35 mole) of m-bis(3,3,3 trifluoropropylmethylhydridosilyl) benzene; yield, 71%; n_D^{25} 1.4404, b.p. 85°C at 0.03 mm of Hg. See Table 2 for properties and analyses.

2. Preparation of m-Bis(3,3,3 trifluoropropylmethylethoxysilyl)benzene

Magnesium (50 g; 2.06 g-atoms) which had been oven dried at 150°C for 1 hour was poured into the pot followed by 600 ml of dry tetrahydrofuran and 904 g (2.67 equiv. of Si-Cl) of a mixture of 3,3,3 trifluoropropylmethyl-ethoxychlorosilane and 3,3,3 trifluoropropylmethyldiethoxysilane. Metadibromobenzene (156.2 g; 0.67 mole) and 300 ml. of dry tetrahydrofuran were mixed in the addition funnel. Approximately 20 ml. of the latter solution was run into the pot, stirred vigorously, and warmed with a hot-air gun. At 47°C an exotherm commenced and in a few minutes the system had warmed to 85°C. Thereafter the rate of addition was regulated to keep the system at 68°C. The addition was completed in 2.7 hours and was followed by 4 hours of additional stirring and heating at 68°C. Tetrahydrofuran was strip-distilled at reduced pressure, 250 ml. of dry hexane was added and the salts were removed by filtration. Distillation gave 198.7 g (66.8%) of crude m-silphenylene which contained both ethoxy and chloro groups, as indicated by NMR; b.p. 106 at 0.25 mm of Hg; n_D^{25} 1.4329.

^1H NMR (60 M Hz) (CCl_4) δ 7.2 - 7.9 (m, 4H, aromatic),
 δ 3.72 (d, 3.44, OCH_2), δ 2.1 (m, 4.5H, CF_3CH_2-), δ 1.16
(s, 8.6H, CH_3-C), δ .68 and .41 (s, 6.1H, CH_3Si).

B. Preparation of m-Bis(trimethylsilyl)benzene

Metallation of m-Dibromobenzene with Metallic Lithium

An oven dried 500 ml 3 necked flask equipped with a magnetic stirrer, condenser, addition funnel, inlet for nitrogen and a thermometer was charged with 5.9 g (0.84 g atom) of lithium wire and 115 ml of dry diethylether. From the addition funnel a solution of 47.1 g of m-dibromobenzene (0.2 mole) in 225 ml of dry diethylether was added dropwise over a period of 1 hour. No evidence of reaction was observed so a few drops of methanol were added. After the reaction started, the system was stirred overnight, followed by the addition of 43.5 g (0.40 mole) of trimethylchlorosilane. The mixture was refluxed (35°C) for 5 hours, stirred overnight, and filtered. GLC-Mass Spectral analysis indicated the following approximate mole percents: 14% $\text{C}_6\text{H}_5\text{Br}$, 38% $\text{Me}_3\text{SiC}_6\text{H}_5$, 13% $\text{mBr}_2\text{C}_6\text{H}_4$, 25% $\text{m}(\text{Me}_3\text{Si})_2\text{C}_6\text{H}_4$ and small amounts of $\text{C}_6\text{H}_5-\text{C}_6\text{H}_5$, $\text{BrC}_6\text{H}_4-\text{C}_6\text{H}_5$, $\text{Me}_3\text{SiC}_6\text{H}_4-\text{C}_6\text{H}_5$, $\text{BrC}_6\text{H}_4-\text{C}_6\text{H}_4\text{Br}$ and $\text{C}_6\text{H}_5-\text{C}_6\text{H}_4-\text{C}_6\text{H}_5$.

The above reaction was repeated with 115 ml of tetrahydrofuran, 6.08 g (0.88 g-atom) of lithium wire and 46.2 g (0.43 m) of trimethylchlorosilane in the pot. A solution of 50.2 g (0.21 m) of m-dibromobenzene in 225 ml of tetrahydrofuran

was added dropwise. An ice bath was employed to control the exotherm. After 4 hours of stirring the products were filtered. GLC indicated a much cleaner reaction with two major products, $\text{BrC}_6\text{H}_4\text{SiMe}_3 / (\text{Me}_3\text{Si})_2\text{C}_6\text{H}_4$, in a ratio of 22/78 respectively which distilled as a mixture; yield 58%.

C. Preparation of m-Bis(trimethylsilyl)benzene.

Metallation of m-Dibromobenzene with n-Butyllithium

The apparatus described in part B was dried in an oven assembled hot, and allowed to cool with dry nitrogen flowing through it. A solution of 33.0 g (0.14 m) of m-dibromobenzene in 60 ml of diethylether was introduced and the pot and contents were cooled in a Dry Ice-Acetone/bath. From the addition funnel a solution of 184 ml of 1.6N n-butyllithium in n-hexane (0.29 m of Li) in 122 ml of diethylether was added dropwise over a period of 50 minutes. Disappearance of m- $\text{Br}_2\text{C}_6\text{H}_4$ was followed by GLC. After 2.5 hours of stirring 32.1 g (0.29 m) of trimethylchlorosilane was added dropwise over a period of 1 hour. After 20 minutes the Dry Ice bath was removed and the products were filtered and analyzed by GLC-Mass Spectroscopy which indicated: 41% $\text{BrC}_6\text{H}_4\text{SiMe}_3$, 41% $(\text{Me}_3\text{Si})_2\text{C}_6\text{H}_4$ and minor amounts of $\text{Me}_3\text{Si-C}_6\text{H}_5$, BuC_6H_5 and $\text{BuC}_6\text{H}_4\text{SiMe}_3$.

When the above reaction was repeated at room temperature a reaction occurred between tetrahydrofuran and n-butyllithium - no silylated benzenes were formed.

D. Preparation of Symmetrical Bis(3,3,3 trifluoropropyl) dimethylbis(N-methylacetamido)disiloxane via Ligand Exchange

Into a dry 25 ml 3 necked flask equipped with a vacuum connection, thermometer, rubber septum and magnetic stirrer 5 ml (0.0175 m) of symmetrical bis(3,3,3 trifluoropropyl)dimethyldichlorodisiloxane was introduced. N-methylacetamidotrimethylsilane (5 ml) was introduced with a dry syringe and the reactants were stirred while a slight vacuum was applied to aid the removal of trimethylchlorosilane. GLC showed the formation of one product.

The above was repeated with 503 g (1.37 moles) of symmetrical bis(3,3,3 trifluoropropyl)dimethyldichlorodisiloxane and 437.0 g (3.01 moles) of N-methylacetamidotrimethylsilane.

The products were distilled to give 450 g (1 mole), 74%, of pure symmetrical bis(3,3,3-trifluoropropyl)bis(N-methylacetamido)dimethyldisiloxane, b.p. 100° at 0.02 mm of Hg, and 68 g of lesser purity (90%). The pure material was identical to that prepared earlier by another route¹⁴.

E. Preparation of Symmetrical Bis(dimethylamino)dimethylbis(3,3,3 trifluoropropyl)disiloxane

A 2 l resin kettle equipped with a Dry Ice condenser, addition funnel, mechanical stirrer and an inlet for dimethylamine or nitrogen and containing 500 ml of dry hexane was cooled by immersion in a Dry Ice - isopropanol mixture. Dimethylamine, 57.8 g (1.28 mole) was condensed in the cold hexane. From the

addition funnel a solution of 92.0 g (0.25 m) of symmetrical bis (3,3,3 trifluoropropyl)dimethyldichlorodisiloxane in 70 ml of dry hexane was added in rapid drops over a period of 50 minutes while the amine solution was stirred. The system was allowed to warm to room temperature where the products were filtered and distilled to give 68 g (0.17 m), 71%, of pure symmetrical bis (3,3,3 trifluoropropyl)bis(dimethylamino)dimethyldisiloxane; b.p. 55° at 0.05 mm of Hg, n_D^{25} 1.3851; $^1\text{H-NMR}$ (90 M Hz) (CCl_4) δ 0.11 (s, 6H, SiMe), [δ 0.81 (m, SiCH_2) + δ 1.98 (m CH_2CF_3) 8H], δ 2.51 (s, 12H, NMe).

F. Preparation of 3,3,3 Trifluoropropylmethyldiethoxy silane

A three liter, three necked flask was equipped with a water-cooled condenser, addition funnel, thermometer, inlet for nitrogen, and a magnetic stirrer. The condenser was vented to two water traps in series. The flask was loaded with 1862 g of a mixture of 3,3,3 trifluoropropylmethyldiethoxysilane, 3,3,3 trifluoropropylmethylethoxychlorosilane and 3,3,3 trifluoropropylmethyldichlorosilane, which by titration contained 10.4 equivalents of Si-Cl. Nitrogen entered the system below the liquid surface. To this mixture 790 g (17.1 moles) of absolute ethanol was added over a period of two hours. The products were kept at 55°C and stirred for 48 hours while nitrogen purged the system of HCl. The products were made slightly basic by the addition of sodium ethoxide in ethanol,

filtered, and distilled to give 1050 g (4.6 moles) of 3,3,3-trifluoromethyldiethoxysilane, 330 g (0.9 mole) of symmetrical bis(3,3,3 trifluoropropyl)dimethyldiethoxydisiloxane and 70 g (0.13 mole) of 1,3,5 tris(3,3,3 trifluoropropyl-1,3,5 trimethyl-1,5 diethoxytrisiloxane. Properties appear in Table 2.

G. Preparation of m-Bis[Methyl(N-methylacetamido)3,3,3-trifluoropropylsilyl]benzene

Utilizing a 50 ml flask and the other equipment and procedures described in part D, 19.6 g (39.3 mmole) of m-bis-(3,3,3 trifluoropropylmethylchlorosilyl)benzene was allowed to react with 11.8 g (0.081 m) of N-methylacetamidotrimethylsilane to produce m-bis[(N-methylacetamido)3,3,3 trifluoropropylmethylsilyl]benzene - 98% pure by GLC. Trimethylchlorosilane was removed by imposing a slight vacuum and warming the pot to 40°C. The crude product was kept in the closed system for subsequent polymerization.

H. Preparation of 1,3 Bis(phenyldimethylureido)bis-(3,3,3 trifluoropropyl)dimethyldisiloxane

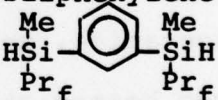
Into a dry vial containing a small magnetic stirring bar and capped with a septum, 5.82 g (15.1 mmole) of symmetrical bis(dimethylamino)bis(3,3,3 trifluoropropyl)dimethyldisiloxane, 2 ml of dry diethylether, and 3.7 g (31.2 mmole) of phenylisocyanate were introduced with a syringe in the above order. The system was stirred overnight. The product was kept under nitrogen while it was washed with hexane and diethylether. The crude product was saved for subsequent polymerization.

I. Preparation of m-Bis(3,3,3 trifluoropropylmethylhydroxysilyl)benzene

1. Via Hydrolysis of Alkoxyfunctional Silphenylene

To a stirred solution of 5.4 g (0.096 m) of potassium hydroxide in 5 ml of water and 40 ml of methanol, 10 g (0.024 m) of m-bis(3,3,3 trifluoropropylmethoxysilyl)benzene in 24 ml. of methanol was added dropwise. After the addition was completed 5.4 g (0.096 m) of potassium hydroxide in 50 ml of water was added slowly. The resulting solution was stirred for 30 minutes and then was added slowly to a stirred solution of 33.1 g (0.24 m) of $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ in 100 ml of water and ice. The resulting mixture was extracted with 2 x 30 ml of diethylether, dried over anhydrous magnesium sulfate, filtered and distilled to give 8.0 g (85.4%) of m-bis(3,3,3 trifluoropropylmethylhydroxy)benzene, n_D^{25} 1.4591, which crystallized. ^1H NMR (60 M H_2), (d_6 acetone); δ 0.40 (s, 6H, SiCH_3); δ 1.02 (m, SiCH_2) + δ 2.20 (m, CH_2CF_3) (8H); δ 5.15 (s, 2H, SiOH); δ 7.0 - 7.8 (m, 4H, arom).

2. Via Hydrolysis of Hydride-Functional Silphenylene

In a 100 ml flask 3.58 g (0.01 m) of 

was combined with 40 ml of dioxane, 10 ml of 0.1N $\text{NaOH}/\text{NaH}_2\text{PO}_4$ buffer solution, and 0.05 g of 5% Pd/C (powder) and stirred for 2 days. Analysis of the mixture by IR indicated complete reaction of SiH . The products were filtered, concentrated

under vacuum, diluted with 100 ml of diethylether and dried over CaSO_4 , filtered, and again concentrated at 0.1 mm of Hg at 35°C to give 4.0 g of viscous fluid which crystallized overnight. NMR indicated 0.27 wt. % H_2O or 6 molecules of water per 100 molecules of bis-silanol.

J. Polymerization Reactions - Preparation of FASIL

1. Reaction of m-Bis(3,3,3 trifluoropropylmethylhydrolysilyl)benzene with Symmetrical bis(N-methylacetamido)bis(3,3,3 trifluoropropyl)dimethyldisiloxane

A one ounce dry, septum vial was loaded with 7.815 g (0.020 m) of m-bis(3,3,3 trifluoropropylmethylhydroxysilyl)benzene and 8.66 g (0.0196 m) of symmetrical bis(N-methylacetamido)bis(3,3,3 trifluoropropyl)dimethyldisiloxane. A slight exotherm occurred accompanied by an increase in viscosity. Heating the system at 35° to 60°C produced a slight increase in viscosity. Additional chain extender (0.03 g) was added and the reactants were heated at 110°C for 3 days. Each day the sample was devolatilized at 0.1 mm of Hg to remove N-methylacetamide, and slight viscosity increases were noted. The fluid was heated at 40°C with 0.3 g of Nuchar filtered hot through a bed of Perlite to give an amber colored fluid, n_D^{25} 1.4225, visc. (Brookfield) 29500 cp. This material was submitted to AFML.

2. Reaction of m-Bis[methyl(N-methylacetamido)
(3,3,3 trifluoropropylsilyl)]benzene with Symmetrical
bis(3,3,3 trifluoropropyl)dimethyldihydroxysiloxane

To the m-silphenylene prepared in part F a solution of 14.2 g (43.1 mmole) of symmetrical bis(3,3,3 trifluoropropyl)dimethyldihydroxydisiloxane in 10 ml of tetrahydrofuran was added via syringe. An exotherm of 30° was observed whereafter the reactants were heated at 95°C at 1 mm of Hg for several days. The fluid was precipitated from toluene by addition of methanol, washed with methanol and devolatilized under vacuum. Characterization data includes: GPC, Mn 1280, Mw 2410, Dispersity 1.88, Peak M 2750; H'NMR (90 M H₂) (d₆ acetone), 0.21, 0.52 (s, 12H, SiMe), 0.93 (m, SiCH₂) + 2.01 (m, CH₂CF₃) (8H), 7.2-7.9 (m, 4H, arom.) - Anal. 135.6 ppm N.

3. Reaction of 1,3 Bis(phenyldimethylureido)bis-
(3,3,3 trifluoropropyl)dimethyldisiloxane with
m-Bis(3,3,3 trifluoropropylmethylhydroxysilyl)
benzene

To the ureido-functional disiloxane prepared in part G 6.43 g (16.5 mmole) of m-bis(3,3,3 trifluoropropylmethylhydroxysilyl)benzene in 4 ml of toluene was added via syringe. The reactants were stirred and heated at 80-110°C for 8 hours. The resulting polymer was precipitated from toluene with methanol, dissolved in diethylether, washed with aqueous sodium bicarbonate and sodium chloride treated with decolorizing carbon and anhydrous calcium sulfate and filtered under vacuum. The polymer was again precipitated from toluene by addition of methanol and devolatilized under vacuum. This sample was submitted to AFML.

4. Reaction of m-Bis(3,3,3 trifluoropropylmethylhydroxysilyl)benzene with Symmetrical Bis-(3,3,3 trifluoropropyl)dimethyldichlorodisiloxane

To a 25 ml., 3 necked blanketed with an atmosphere of nitrogen 6.04 g (15.5 mmole) of m-bis(3,3,3 trifluoropropylmethylhydroxysilyl)benzene and 5.64 g (14.5 mmole) of symmetrical bis(3,3,3 trifluoropropyl)dimethyldichlorodisiloxane were added. An exotherm of 30° occurred and afterwards the system was stirred and heated at 90°-135°C for 24 hours. The polymer was dissolved in ether, washed with aqueous sodium bicarbonate and sodium chloride, dried with calcium sulfate, filtered and devolatilized. The viscosity was low so 2 drops of tetramethylguanidine trifluoroacetate (1:3) was added followed by heating at 110°C at 90 mm of Hg for 3.5 hours. The polymer had increased in viscosity. It was washed as above, treated with decolorizing carbon, dried with anhydrous calcium sulfate, filtered and devolatilized. This material was submitted to AFML.

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


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TABLE 1
RESULTS OF GRIGNARD REACTIONS

REFERENCE	REACTANTS - MOLES						Solvent		Conditions		PRODUCT - YIELD (M%)		
	$\text{A} \cdot 10^3$	$\text{B} \cdot 10^3$	$\text{C} \cdot 10^3$	$\text{D} \cdot 10^3$	$\text{E} \cdot 10^3$	$\text{F} \cdot 10^3$	THF	THF/RA	TIME (hr)	TEMP (°C)	$\text{A} \cdot 10^3$	$\text{B} \cdot 10^3$	TOTAL
10	0.33	4.00	(OEt) ₂	50	0.73	10	7.2	11	7.0	62-70	17.0	44.7	63.7
19	0.33	4.00	(OEt) ₂	50	0.80	21	7.2	11	6.0	55-70	17.1	62.8	71.9
25	0.33	1.33	(OEt) ₂	100	0.80	21	7.2	11	17.0	40-70	12.1	56.5	68.6
42	0.44	2.44	(OEt) ₂	100	2.00	50	14.4	11	8.0	50-85	15.2	42.9	58.1
48	0.44	2.44	(OEt) ₂	100	2.00	50	21.6	16.4	5.5	55-85	6.1	66.8	72.9
52	0.33	1.00	(OMe) ₂	50	0.80	21	7.2	11	5.0	55-70	9.1	45.0	54.1
57	0.66	2.44	(OMe) ₂	100	2.00	50	21.6	16.4	3.0	60-80	7.5	56.0	63.5
65	0.44	2.44	(OMe) ₂	100	2.00	50	15.9	12	5.0	45-62	13.4	57.1	72.5
82	0.66	2.44	(OMe) ₂	100	2.00	50	11.0	8.3	4.5	50-66	COMBINED RUNS 10.0		
84	0.66	2.44	(OMe) ₂	100	2.00	50	11.0	8.3	4.5	50-65		53.0	63.0
86	0.66	2.44	(OMe) ₂	100	2.00	50	10.5	8.0	5.0	52-65			
74	0.50	2.00	(OEt) ₂	100	1.50	50	16.4	16.4	4.5	55-67	14.0	70.9	84.9
78	0.50	2.00	(OEt) ₂	100	2.00	100	16.4	16.4	4.5	55-63	16.8	65.4	82.4
119	0.15	0.60	(OEt) ₂	100	0.50	50	2.4	8.0	2.0	50-60	11.3	55.0	66.3
92	0.15	0.60	(N)Cl	100	0.50	50	2.4	8.0	3.0	45-55	---	75.0	75.0
96	0.15	0.60	(N)Cl	100	0.50	50	2.4	8.0		40-58	NORMAL + ADDITION	43.5	43.5
100	0.15	0.60	(N)Cl	100	0.50	50	2.4	8.0	2.0	25-34		70.0	70.0
104	0.15	1.20	(N)Cl	200	0.50	50	2.4	8.0	2.5	22-32	---	78.0	78.0
115	0.50	3.00	(N)Cl	200	1.50	50	8.1	8.0	3.0	18-24	---	64.0	64.0
122	0.10	1.20	(N)Cl	500	0.30	50	1.6	8.0	1.5	18-22	---	80.0	80.0
128	0.15	0.90	(N)Cl	200	0.45	50	(same) 2.4	8.0	8.0	28-47	---	49.3	49.3
132	0.50	3.00	(N)Cl	200	1.50	50	8.4	8.4	3.5	15-19	---	74.0	74.0
138	1.00	6.00	(N)Cl	200	3.00	50	16.0	8.0	4.5	14-17	---	76.0	76.0
144	0.15	1.20	(N)Cl	200	0.45	50	2.4	8.0	3.5	15-17	---	73.0	73.0
148	0.50	3.00	(N)Cl	200	1.50	50	8.4	8.4	2.5	15-17	---	70.3	70.3
235H-25	0.15	1.20	(N)Cl	200	0.45	50	2.4	8.0	2.5	15-16	---	62.0	62.0
28	0.15	0.45	Cl ₂	200	0.45	50	2.4	8.0	4.0	14-18	27.1	61.9	89.0
34	0.50	1.50	Cl ₂	300	1.50	50	8.0	8.0	6.0	14-18	26.7	57.0	85.7

* "IN-SITU" TECHNIQUE USED IN ALL OTHER RUNS

TABLE 2. COMPOUNDS

Compound	Boiling Point	n_D^{25}	Density	Specific Refraction (R _D)	% Si	% F	H ¹ NMR (90M H ₂) (CCl ₄)
				Calcd.	Found	Calcd.	Found
$\begin{array}{c} \text{Pr}_f \\ \\ \text{EtO}-\text{Si}-\text{Me} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Si}-\text{OEt} \\ \\ \text{Pr}_f \end{array}$	95-100 ^{0.005} 135.0 ^{1.0}	1.4338	1.1240 ²⁵	0.2291 0.2316	12.5% 11.4 ^{±0.3}	25.6% 26.3 ^{±0.3}	7.2-7.9 (m, 4H, ) 3.76 (m, 4H, OCH ₂) 2.1 (m, 4H, CF ₃ CH ₂) (m, 10H, SiCH ₂ +C-CH ₃) 1.2 (m, CH ₃) 0.37 (s, 6H, SiCH ₃)
$\begin{array}{c} \text{Pr}_f \\ \\ \text{MeO}-\text{Si}-\text{Me} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Si}-\text{OMe} \\ \\ \text{Pr}_f \end{array}$	100-105 ^{0.03}	1.4359	1.1703 ²⁵	0.2222 0.2234	13.43% 14.6 ^{±0.4}	27.3% 24.8 ^{±0.3}	7.2-7.8 (m, 4H, ) 2.1 (m, 4H, CF ₃ CH ₂) 1.0 (m, 4H, SiCH ₂) 0.46 (s, 6H, SiCH ₃) 3.48 (s, 6H, OCH ₃)
$\begin{array}{c} \text{Pr}_f \\ \\ \text{H}-\text{Si}-\text{Me} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Si}-\text{H} \\ \\ \text{Pr}_f \end{array}$	85 ^{0.03}	1.4412	1.1317 ²⁵	0.2291 0.2334	15.60% 16.0 ^{±0.5}	31.67% 33.0 ^{±1.8}	7.1-7.8 (m, 4H, ) 2.1 (m, 4H, CF ₃ CH ₂) 1.07 (m, 4H, SiCH ₂) 0.37 (d, 6H, SiCH ₃) 4.47 (m, 2H, SiH)
$\begin{array}{c} \text{Me} \\ \\ \text{Pr}_f-\text{Si}-\text{OEt} \\ \\ \text{O} \\ \\ \text{Et} \end{array}$	152 ⁷⁴⁴ 301.5	1.3598	1.0283 ²⁵	0.2160 0.2145	12.2% 12.3 ^{±0.3}	24.8% 24.2 ^{±0.5}	3.72 (m, 4H, OCH ₂) 2.04 (m, 2H, CF ₃ CH ₂) 0.74 (m, 2H, SiCH ₂) 0.07 (s, 3H, SiCH ₃) 1.17 (m, 6H, CH ₃)
$\begin{array}{c} \text{Me} \\ \\ \text{Pr}_f-\text{Si}-\text{O}-\text{Si}-\text{Pr}_f \\ \quad \\ \text{OEt} \quad \text{OEt} \end{array}$	79 ^{1.0}	1.3672	1.1161 ²⁵	0.1994 0.2013	14.53% 14.3 ^{±0.4}	29.5% 29.6 ^{±0.5}	3.71 (m, 4H, OCH ₂) 2.07 (m, 4H, CF ₃ CH ₂) 0.75 (m, 4H, SiCH ₂) 0.11 (s, 6H, SiCH ₃) 1.18 (m, 6H, CCH ₃)
$\begin{array}{c} \text{Me} \quad \text{Me} \\ \quad \\ \text{EtO}-\text{Si}-\text{O}-\text{Si}-\text{OEt} \\ \quad \quad \quad \\ \text{Pr}_f \quad \text{Pr}_f \quad \text{Pr}_f \quad \text{Pr}_f \end{array}$	120 ^{1.0}	1.3708	1.1627 ²⁵	0.1923 0.1949	15.53% 15.4 ^{±0.4}	31.5% 31.4 ^{±0.5}	3.74 (m, 4H, OCH ₂) 2.06 (m, 6H, CF ₃ CH ₂) 0.76 (m, 6H, SiCH ₂) 0.16 (s, 9H, SiCH ₃) 1.20 (m, 6H, CCH ₃)

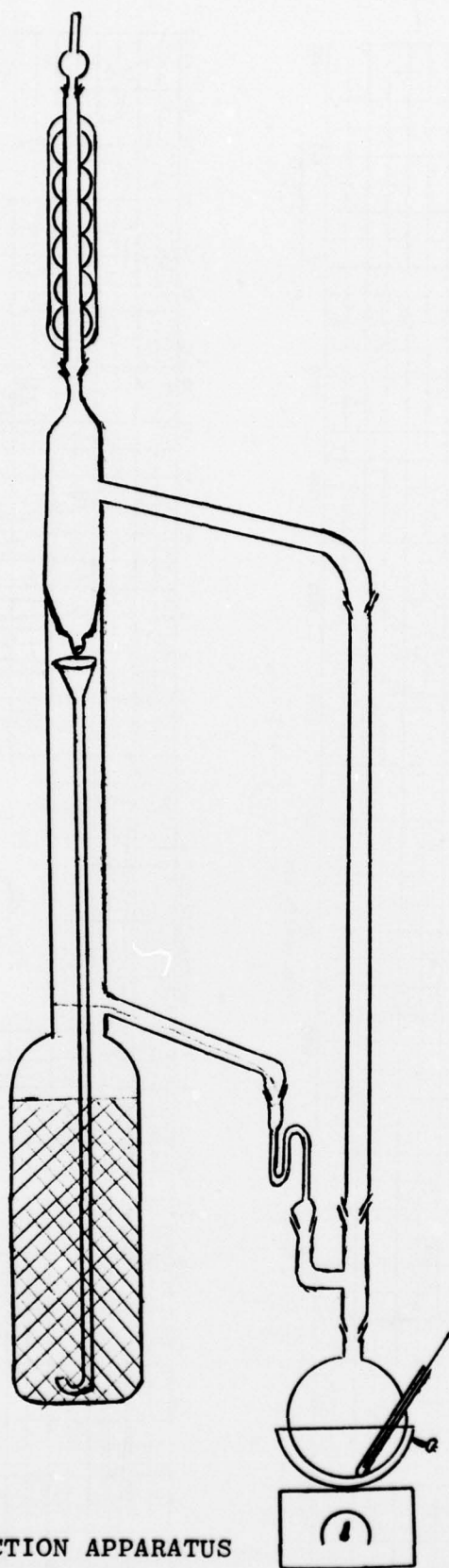


FIGURE 1. EXTRACTION APPARATUS

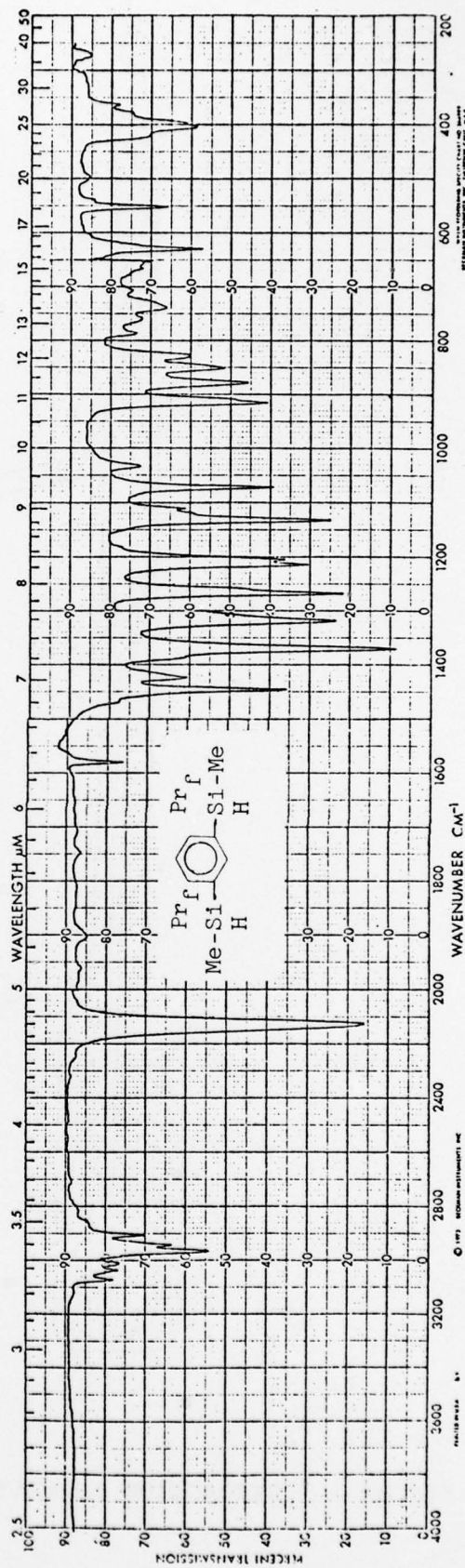
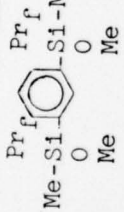
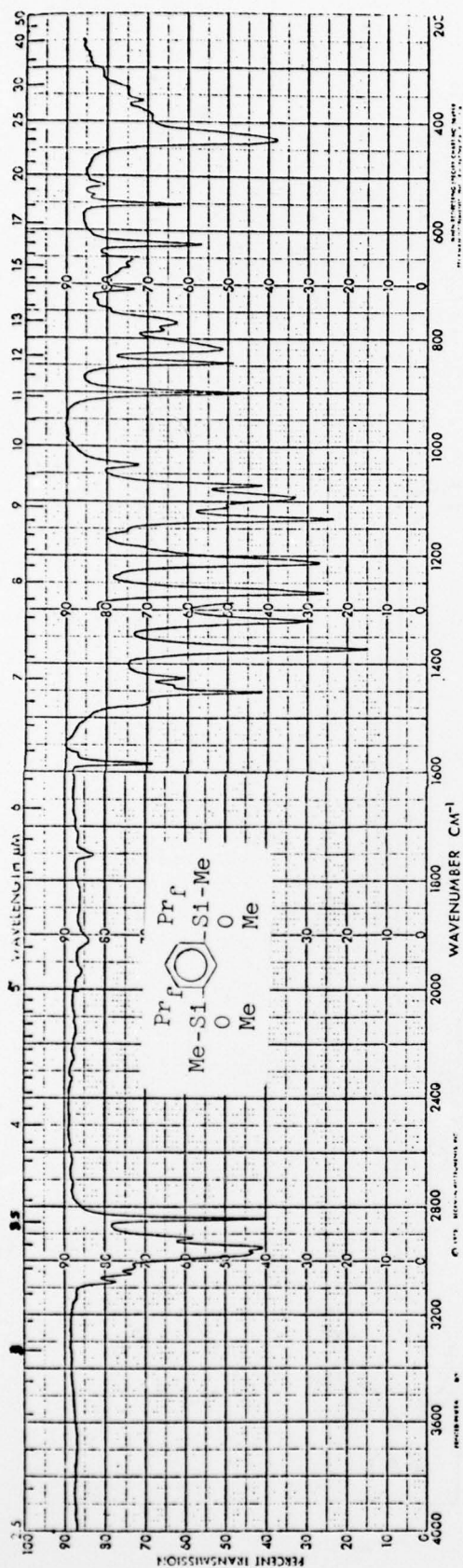


FIGURE 2. INFRARED SPECTRA